

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-167937

(43)Date of publication of application : 22. 06. 1999

---

(51) Int. Cl.

H01M 14/00

H01L 31/04

---

(21)Application number : 10-241839 (71)Applicant : FUJI PHOTO FILM CO  
LTD

(22)Date of filing : 27. 08. 1998 (72)Inventor : KOBAYASHI KATSU  
HIOKI TAKANORI  
YAMASHITA KATSUHIRO  
WATANABE TETSUYA  
KATO TAKASHI

---

(30)Priority

Priority	09267455	Priority	30. 09. 1997	Priority	JP
number :	09281187	date :	30. 09. 1997	country :	JP

---

(54) PHOTOELECTRIC TRANSFER ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an element having high transfer efficiency by adsorbing organic pigment such that the pigment coloring groups exist in a plurality in the vertical direction to surfaces of semiconductor particulates and forming a metallic polynuclear complex part as a single coloring group.

SOLUTION: Semiconductor particulates sensitized by simultaneously using at least one kind of methine pigment of formula I and at least one kind of methine pigment of formula II are preferably used. In formulas I and II, Z1 and Z2 represent an atomic group required to form a nitrogen-containing heterocycle and R1 and R2 represent an alkyl group or an aryl group and Q1 and Q2 represent a methine group or a polymethine group required to form methine pigment by a compound respectively expressed by formulas I and II and L1 to L4 represent a methine group and p1 and p2 represent 0 or 1. Here, Z1, R1 and Q1 have a substitutional group becoming

cation pigment by methine pigment expressed by formula I and Z<sub>2</sub>R<sub>2</sub> and Q<sub>2</sub> have a substitutional group becoming anion pigment by methine pigment of the formula II. M<sub>1</sub> and M<sub>2</sub> represent respectively electric charge balanced anion and cation. Symbols m<sub>1</sub> and m<sub>2</sub> represent the number 0 to 10 required to neutralize electric charge of a molecule.

---

## CLAIMS

---

[Claim(s)]

[Claim 1] An optoelectric transducer wherein organic coloring matter is adsorbing so that it may be an optoelectric transducer using a semiconductor particulate by which sensitization was carried out and two or more coloring matter chromophoric groups may exist perpendicularly to the semiconductor particulate surface with organic coloring matter. However let a metal polynuclear complex portion be one chromophoric group. However let a metal polynuclear complex portion be one chromophoric group.

[Claim 2] The optoelectric transducer according to claim 1 using a semiconductor particulate by which sensitization was carried out in cation coloring matter by using a kind for a kind and anion coloring matter simultaneously at least.

[Claim 3] Claim 1 using a semiconductor particulate by which sensitization was carried out by using a kind simultaneously at least among methine coloring matter expressed with a kind and following general formula (II) at least among methine coloring matter expressed with following general formula (I) or an optoelectric transducer given in two.

General formula (I)

[Formula 1]

Z<sub>1</sub> expresses an atomic group required to form nitrogen-containing heterocycle among a formula. R<sub>1</sub> is an alkyl group or an aryl group. Q<sub>1</sub> expresses a methine group required for the compound expressed with general formula (I) to form methine coloring matter or a poly methine group. L<sub>1</sub> and L<sub>2</sub> express a methine group. p<sub>1</sub> expresses 0 or 1. However Z<sub>1</sub>, R<sub>1</sub> and Q<sub>1</sub> shall have a substituent from which the methine coloring matter expressed with general formula (I) turns into cation coloring matter as a whole. M<sub>1</sub> expresses the negative ion for electric charge balance and m<sub>1</sub> expresses or more 0 ten or less number required to neutralize the electric charge of a molecule.

General formula (II)

[Formula 2]

$Z_2$  expresses an atomic group required to form nitrogen-containing heterocycle among a formula.  $R_2$  is an alkyl group or an aryl group.  $Q_2$  expresses a methine group required for the compound expressed with general formula (II) to form methine coloring matter or a poly methine group.  $L_3$  and  $L_4$  express a methine group.  $p_2$  expresses 0 or 1. However  $Z_2R_2$  and  $Q_2$  shall have a substituent from which the methine coloring matter which is general formula (II) and is expressed turns into anion coloring matter as a whole.  $M_2$  expresses the positive ion for electric charge balance and  $m_2$  expresses or more 0 ten or less number required to neutralize the electric charge of a molecule.

[Claim 4] The optoelectric transducer according to claim 1 using a semiconductor particulate of a compound with two or more coloring matter portions connected by a covalent bond by a divalent connecting group in which sensitization was carried out by kind at least.

[Claim 5] The optoelectric transducer according to claim 1 or 4 using a semiconductor particulate of a compound expressed with following general formula (III) in which sensitization was carried out by kind at least.

General formula (III) [Formula 3]

D expresses among a formula the sensitizing dye portion which sticks to a semiconductor particulate. L expresses a divalent connecting group or single bond. A expresses the luminescent coloring matter portion connected with D by the connecting group L. n may be one or more integers and two or more L and A in which the case of two or more is included may be different connecting groups and luminescent coloring matter portions respectively.

[Claim 6] A photogalvanic cell using an optoelectric transducer of claim 1, 2, 3, 4 or 5.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optoelectric transducer using the semiconductor particulate by which sensitization

was carried out with coloring matter in detail about an optoelectric transducer.

[0002]

[Description of the Prior Art]The optoelectric transducer is used for various kinds of photosensorsthe copying machineand the optical power plant. Various methodssuch as what used metala thing using a semiconductor a thing using an organic color or coloring matteror a thing that combined theseare put in practical use by the optoelectric transducer. On a U.S. Pat. No. 4927721 itemNo. 4684537No. 5084365No. 5350644No. 5463057No. 5525440and JP7-249790A specifications. The material and production technology for creating the optoelectric transducer (it abbreviates to a dye sensitizing optoelectric transducer henceforth) using the semiconductor particulate by which sensitization was carried out with coloring matteror this are indicated. Since the first advantage of this method can be used without refining cheap oxide semiconductorssuch as a titanium dioxideto a high gradeit is at the point that a comparatively cheap optoelectric transducer can be provided. Since broadcloth [ the second advantage / absorption of the coloring matter used ]it is that the light of almost all the wavelength areas of visible light is convertible for the electrical and electric equipment. Since these features are advantageous when they apply solar energy to the optoelectric transducer (what is called a photogalvanic cell) aiming at changing into the electrical and electric equipmentthe application to this direction is considered actively.

[0003]Using the ruthenium complex coloring matter of the point that improvement of a dye sensitizing optoelectric transducer is called for expensive [ one ]as sensitizing dye is mentioned. Although development of the optoelectric transducer by which sensitization is carried out with cheap organic coloring matter was desiredsince the adsorptivity of organic coloring matter to the titanium dioxide was low and the amount of adsorption was smallhigh sensitization efficiency was not able to be obtained.

[0004]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the dye sensitizing optoelectric transducer which has high conversion efficiency.

[0005]

[Means for Solving the Problem]In order to obtain high sensitization efficiencyit is required to raise a light absorption rate per unit surface area. It is required to raise adsorption density of sensitizing dye for that purpose. We developed a method of raising adsorption

density of sensitizing dye as a result of research. That is the purpose of this invention was attained by (1) to (6) shown below.

(1) An optoelectric transducer wherein organic coloring matter is adsorbing so that it may be an optoelectric transducer using a semiconductor particulate by which sensitization was carried out and two or more coloring matter chromophoric groups may exist perpendicularly to the semiconductor particulate surface with organic coloring matter.

However let a metal polynuclear complex portion be one chromophoric group.

[0006] (2) An optoelectric transducer given in (1) characterized by using a semiconductor particulate by which sensitization was carried out in cation coloring matter by using a kind for a kind and anion coloring matter simultaneously at least.

[0007] (3) An optoelectric transducer (1) using a semiconductor particulate by which sensitization was carried out by using a kind simultaneously at least among methine coloring matter expressed with a kind and following general formula (II) at least among methine coloring matter expressed with following general formula (I) or given in (2).

General formula (I)

[0008]

[Formula 4]

[0009]  $Z_1$  expresses an atomic group required to form nitrogen-containing heterocycle among a formula.  $R_1$  is an alkyl group or an aryl group.  $Q_1$  expresses a methine group required for the compound expressed with general formula (I) to form methine coloring matter or a poly methine group.  $L_1$  and  $L_2$  express a methine group.  $p_1$  expresses 0 or 1.

However  $Z_1$ ,  $R_1$  and  $Q_1$  shall have a substituent from which the methine coloring matter expressed with general formula (I) turns into cation coloring matter as a whole.  $M_1$  expresses the negative ion for electric charge balance and  $m_1$  expresses 0 or more 10 or less number required to neutralize the electric charge of a molecule.

General formula (II)

[0010]

[Formula 5]

[0011]  $Z_2$  expresses an atomic group required to form nitrogen-containing heterocycle among a formula.  $R_2$  is an alkyl group or an aryl group.  $Q_2$  expresses a methine group required for the compound expressed with general formula (II) to form methine coloring matter or a poly methine

group.  $L_3$  and  $L_4$  express a methine group.  $p_2$  expresses 0 or 1. However  $Z_2R_2$  and  $Q_2$  shall have a substituent from which the methine coloring matter which is general formula (II) and is expressed turns into anion coloring matter as a whole.  $M_2$  expresses the positive ion for electric charge balance and  $m_2$  expresses or more 0 ten or less number required to neutralize the electric charge of a molecule.

[0012] (4) divalent -- a connecting group -- a covalent bond -- having connected -- two -- a \*\* -- more than -- coloring matter -- a portion -- having -- a compound -- at least -- a kind -- sensitization -- carrying out -- having had -- a semiconductor particulate -- using -- things -- the feature -- carrying out -- (-- one --) -- a statement -- an optoelectric transducer .

[0013] (5) An optoelectric transducer (1) or given in (4) using a semiconductor particulate of a compound expressed with following general formula (III) in which sensitization was carried out by kind at least.

General formula (III) [0014]

[Formula 6]

[0015] D expresses among a formula the sensitizing dye portion which sticks to a semiconductor particulate. L expresses a divalent connecting group or single bond. A expresses the luminescent coloring matter portion connected with D by the connecting group L. n may be one or more integers and two or more L and A in which the case of two or more is included may be different connecting groups and luminescent coloring matter portions respectively.

[0016] The photogalvanic cell using the optoelectric transducer of (6) (1) (2) (3) (4) or (5).

[0017]

[Embodiment of the Invention] This invention is an optoelectric transducer using the semiconductor particulate by which sensitization was carried out with organic coloring matter and is an optoelectric transducer wherein organic coloring matter is adsorbing so that two or more coloring matter chromophoric groups may exist perpendicularly to the semiconductor particulate surface. organic coloring matter is adsorbing so that two or more coloring matter chromophoric groups may exist perpendicularly to the semiconductor particulate surface -- that is it means that the coloring matter chromophoric group has covered the semiconductor particulate surface top to the multilayer. Such an adsorbed state may be formed by what kind of method. With the chromophoric group who stated here a silicification study dictionary (the

fourth edition Iwanami Shoten 1987) and all the atom groups to whom it is shown [ 985-986-page ] by explanation of the chromophoric group of a statement are included.

[0018] This invention showed two methods of having realized still such a coloring matter adsorbed state. One is the method of using together cation coloring matter and anion coloring matter. As long as the coloring matter used for this method is the organic coloring matter which just carried out electrification and the organic coloring matter which carried out electrification to negative what kind of thing may be sufficient as it. As organic coloring matter a spiro compound, metallocene, fluorenone, fulgide, imidazole, perylene, phenazine, phenothiazine, polyene, an azo compound, a disazo compound, quinone, indigo, diphenylmethane, triphenylmethane, poly methine, an acridine, AKURIJINON, carbo styryl, a coumarin, diphenylamine, quinacridone, kino FUTARON, phenoxazine, phtalo perylene, porphyrin, chlorophyll, phthalocyanine, SUKUARIUM, diazobenzene, a bipyridine metal complex (example of a metal polynuclear complex) etc. are mentioned. Preferably an azo compound, diphenylmethane, triphenylmethane, poly methine, porphyrin, phthalocyanine, SUKUARIUM, a bipyridine metal complex etc. are mentioned. It is a time of being poly methine coloring matter which can express with said general formula (I) still more preferably as cation coloring matter. It is a time of general formula (I) being preferably expressed with following general formula (IV).

General formula (IV)

[0019]

[Formula 7]

[0020]  $L_5L_6L_7L_8L_9L_{10}$  and  $L_{11}$  express a methine group among general formula (IV).  $p_3$  and  $p_4$  express 0 or 1.  $n_1$  expresses 0, 1, 2 or 3.  $Z_3$  and  $Z_4$  express an atomic group required in order to form the nitrogen-containing heterocycle of 5 or 6 members.  $R_3$  and  $R_4$  express an alkyl group or an aryl group. At least one side expresses the alkyl group replaced by the aryl group, the aryl group or the heterocycle group among  $R_3$  and  $R_4$ . However  $R_3$  and  $R_4$  do not have an anionic substituent either.  $Z_3Z_4L_3L_4$  and  $L_5$  may be replaced and those substituents do not have an anionic substituent.  $M_3$  expresses the negative ion for electric charge balance and  $m_3$  expresses or more 0 ten or less number required to neutralize the electric charge of a molecule.

[0021] It is a time of being poly methine coloring matter which can

express with said general formula (II) still more preferably as anion coloring matter. It is a time of general formula (II) being preferably expressed with following general formula (V).

General formula (V)

[0022]

[Formula 8]

[0023]  $L_{12}L_{13}L_{14}L_{15}L_{16}L_{17}$  and  $L_{18}$  express a methine group among general formula (V).  $p_5$  and  $p_6$  express 0 or 1.  $n_2$  expresses 0, 1 or 3.  $Z_5$  and  $Z_6$  express an atomic group required in order to form the nitrogen-containing heterocycle of 5 or 6 members.  $R_5$  and  $R_6$  express an alkyl group or an aryl group. At least one side expresses the alkyl group replaced by the aryl group, the aryl group or the heterocycle group among  $R_5$  and  $R_6$ . However  $R_5$  and  $R_6$  have an anionic substituent.  $M_4$  expresses the negative ion for electric charge balance and  $m_4$  expresses 0 or more, 10 or less number required to neutralize the electric charge of a molecule.

[0024] Another method of having realized an adsorbed state that a coloring matter chromophoric group had covered a semiconductor particulate surface top to a multilayer is a method of using a pigment compound with two or more coloring matter chromophoric group portions connected by a covalent bond by a divalent connecting group. As a coloring matter chromophoric group who can use what kind of thing may be used. As a coloring matter chromophoric group a spiro compound, metallocene, fluorenone, fulgide, imidazole, perylene, phenazine, phenothiazine, polyene, an azo compound, a disazo compound, quinone, indigo, diphenylmethane, triphenylmethane, poly methine, an acridine, AKURI, JINON, carbo styryl, a coumarin, diphenylamine, Quinacridone, kino, FUTARON, phenoxazine, phtalo perylene, porphyrin, chlorophyll, phthalocyanine, SUKUARIUM, diazobenzene, a bipyridine metal complex, etc. are mentioned. Preferably an azo compound, diphenylmethane, triphenylmethane, poly methine, porphyrin, phthalocyanine, SUKUARIUM, a bipyridine metal complex, etc. are mentioned.

[0025] It is a time of being poly methine coloring matter expressed with said general formula (III) as desirable connection coloring matter. In said general formula (III) it is a time of being methine coloring matter by which D and A are independently expressed with following general formula (VI) (VII) or (VIII) respectively still more preferably.

General formula (VI)

[0026]



[Formula 9]

[0027]  $L_{19}L_{20}L_{21}L_{22}L_{23}L_{24}$  and  $L_{25}$  express a methine group among formula (VI).  $p_7$  and  $p_8$  express 0 or 1.  $n_3$  expresses 012 or 3.  $Z_7$  and  $Z_8$  express an atomic group required in order to form the nitrogen-containing heterocycle of 5 or 6 members.  $M_5$  expresses an electric charge equilibrium counter ion and  $m_5$  expresses or more 0 four or less number required to neutralize the electric charge of a molecule.  $R_7$  and  $R_8$  express an alkyl group.

General formula (VII) [0028]

[Formula 10]

[0029]  $L_{26}L_{27}L_{28}$  and  $L_{29}$  express a methine group among formula (VII).  $p_9$  expresses 0 or 1.  $n_4$  expresses 012 or 3.  $Z_9$  and  $Z_{10}$  express an atomic group required in order to form nitrogen-containing heterocycle of 5 or 6 members.  $M_6$  expresses an electric charge equilibrium counter ion and  $m_6$  expresses or more 0 four or less number required to neutralize an electric charge of a molecule.  $R_9$  and  $R_{10}$  express an alkyl group an aryl group or a heterocycle group.

General formula (VIII) [0030]

[Formula 11]

[0031] Formula (VIII)  $NakaL_{30}L_{31}L_{32}L_{33}L_{34}L_{35}L_{36}L_{37}$  and  $L_{38}$  express a methine group.  $p_{10}$  and  $p_{11}$  express 0 or 1.  $n_5$  and  $n_6$  express 012 or 3.  $Z_{11}Z_{12}$  and  $Z_{13}$  express an atomic group required in order to form the nitrogen-containing heterocycle of 5 or 6 members.  $M_7$  expresses an electric charge equilibrium counter ion and  $m_7$  expresses or more 0 four or less number required to neutralize the electric charge of a molecule.  $R_{11}$  and  $R_{13}$  express an alkyl group.  $R_{12}$  expresses an alkyl group an aryl group or a heterocycle group.

[0032] Hereafter a methine compound expressed with general formula (I) and (II) is described in detail.  $Q_1$  and  $Q_2$  express a methine group required to form methine coloring matter or a poly methine group among general formula (I) and (II). the number of methine in a poly methine group -- desirable -- 0 to 9 -- further -- desirable -- 1 to 7 -- it is 3 to 7 especially preferably. When a methine group is included in heterocycle a methine group may be seemingly set to 0. For example simple merocyanine (zero methine merocyanine) is mentioned. If methine coloring matter is formed  $Q_1$  and  $Q_2$  Although what kind of thing may be used it is a

substitution methine group required to form methine coloring matter preferably or a poly methine group and an aromatic group a heterocycle group an amino group a cyano group an alkoxy carbonyl group an alkyl sulfonyl group an acyl group etc. are mentioned as such a substituent. Specifically as an aromatic group an aromatic group (for example 4-dimethylaminophenyl 4-methoxyphenyl 4-dimethylamino naphthyl) etc. which is not replaced [ substitution or ] are mentioned. A basic core publicly known as heterocycle of a heterocycle group when forming coloring matter and an acidic nucleus are mentioned. Specifically A thiazoline core a thiazole core a benzothiazole core an oxazoline core an oxazol core a benzoxazol core a selenazoline core a selenazole core a benzoselenazole nucleus a 3,3-dialkyl INDO renin core (for example 3,3-dimethyl INDO renin) An imidazoline nucleus an imidazole nucleus a benzimidazole core 2-pyridine core 4-pyridine core 2-quinoline core 4-quinoline core 1-isoquinoline core 3-isoquinoline core imidazo [4,5-b] A quinoxaline core an oxadiazole core a thiadiazole core a tetrazole core a pyrimidine base etc. can be mentioned. As an amino group an amino group (for example amino \*\* dimethylamino) which is not replaced [ substitution or ] is mentioned. As an alkoxy carbonyl group an alkoxy carbonyl group (for example ethoxy carbonyl) which is not replaced [ substitution or ] is mentioned. As an alkyl sulfonyl group an alkyl sulfonyl group (for example methanesulfonyl) which is not replaced [ substitution or ] is mentioned. As an acyl group an acyl group (for example acetyl) which is not replaced [ substitution or ] is mentioned. By Q<sub>1</sub> and Q<sub>2</sub> although it is also possible to form what kind of methine coloring matter a compound which are general formula (I) and (II) and is expressed Cyanine dymerocyanine dyerhoda cyanine dye 3 core merocyanine dye AROPORA coloring matter a hemicyanine dye a styryl pigment etc. are mentioned preferably. Under the present circumstances a substituent on a methine chain which forms coloring matter also contains in cyanine dye a thing in which a SUKUARIUMU ring and a crocodile NIUMU ring were formed. About details of these coloring matter. F. M. Harmer (F. M. Harmer) work "heterocyclic party UNZU Cyanine Dyes and Related Compounds (Heterocyclic Compounds-Cyanine Dyes.) and Related Compounds" John Willie and Sons (John Wiley & Sons)-New York London 1964 annual publications Day em Sturmer (D. M. Sturmer). Work "heterocyclic Compounds-Special topics in heterocyclic chemistry (Heterocyclic Compounds-Special topics in heterocyclic chemistry)" It is indicated to Chapter 18 Section 14 and the 482nd to 515 pages etc. As for a general formula of cyanine dymerocyanine dye and rhoda cyanine dye what is shown in U.S. Pat. No. 5340694 21st 22-page (XI) (XII) and (XIII) is preferred.

[0033]  $Z_1Z_2Z_3Z_4Z_5$  and  $Z_6$  express an atomic group required to form nitrogen-containing heterocycle among general formula (I) general formula (II) general formula (IV) and general formula (V).  $Z_1Z_2Z_3Z_4Z_5$  As nitrogen-containing heterocycle formed of  $Z_6$  and a thiazoline coreA thiazole coreA benzothiazole corean oxazoline corean oxazol coreA benzooxazol corea selenazoline corea selenazole corebenzoselenazole nucleusA 33-dialkyl INDO renin core (for example 33-dimethyl INDO renin) an imidazoline nucleus an imidazole nucleus a benzimidazole core2-pyridine core4-pyridine core2-quinoline core4-quinoline core1-isoquinoline core3-isoquinoline coreimidazo [45-b] Although a quinoxaline corean oxadiazole corea thiadiazole corea tetrazole corea pyrimidine base etc. can be mentioned Preferably A benzothiazole corea benzooxazol corea 33-dialkyl INDO renin core (for example 33-dimethyl INDO renin) A benzimidazole core2-pyridine core4-pyridine core2-quinoline core1-4-quinoline core1-isoquinoline coreand 3-isoquinoline coreand they are a benzothiazole corea benzooxazol corea 33-dialkyl INDO renin core (for example 33-dimethyl INDO renin) and a benzimidazole core still more preferably.

[0034] If a substituent on  $Z_1Z_2Z_3Z_4Z_5$  and  $Z_6$  is set to V Although there is no restriction in particular as a substituent shown by V for example A halogen atom (For example chlorine bromine iodine and fluoride) a sulfhydryl group a cyano group a carboxyl group a phosphate group a sulfonic group a hydroxy group and the carbon numbers 1-10 -- desirable -- the carbon numbers 2-8 -- further -- desirable -- a carbamoyl group (for example methyl carbamoyl.) of the carbon numbers 2-5 ethyl carbamoyl mol HORINOKAROBONIRU and the carbon numbers 0-10 -- desirable -- the carbon numbers 2-8 -- further -- desirable -- a sulfamoyl group (for example methyl sulfamoyl.) of the carbon numbers 2-5 ethyl sulfamoyl piperidino sulfonyl a nitro group and the carbon numbers 1-20 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- an alkoxy group (for example methoxy.) of the carbon numbers 1-8 ethoxy \*\*2-methoxy ethoxy 2-phenylethoxy and the carbon numbers 6-20 -- desirable -- the carbon numbers 6-12 -- further -- desirable -- an aryloxy group (for example phenoxyp-methylphenoxyp-chlorophenoxynaphthoxy) of the carbon numbers 6-10 [0035] the carbon numbers 1-20 -- desirable -- the carbon numbers 2-12 -- further -- desirable -- an acyl group (for example acetyl.) of the carbon numbers 2-8 benzoyl trichloroacetyl and the carbon numbers 1-20 -- desirable -- the carbon numbers 2-12 -- further -- desirable -- an acyloxy group (for example acetyloxy.) of the carbon numbers 2-8 benzoyloxy one and the carbon numbers 1-20 -- desirable -- the carbon numbers 2-12 -- further -- desirable -- the acylamino group

(for example acetyl amino) of the carbon numbers 2-8. the carbon numbers 1-20 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- a sulfonyl group (for example methanesulfonyl.) of the carbon numbers 1-8 ethanesulfonyl benzenesulphonyl and the carbon numbers 1-20 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- a sulfinyl group (for example methanesulfinyl.) of the carbon numbers 1-8 ethanesulfinyl benzenesulfinyl and the carbon numbers 1-20 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- a sulfonylamino group (for example methanesulfonylamino ethane sulfonylamino benzenesulphonyl amino) of the carbon numbers 1-8 [0036] an amino group and the carbon numbers 1-20 -- desirable -- the carbon numbers 1-12 -- further -- desirable -- a substituted amino group (for example methyl amino.) of the carbon numbers 1-8 Dimethylamino benzyl amino anilinodiphenyl amino the carbon numbers 0-15 -- desirable -- the carbon numbers 3-10 -- further -- desirable -- ammonium (for example trimethyl ammonium.) of the carbon numbers 3-6 triethyl ammonium and the carbon numbers 0-15 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- a hydrazino group (for example trimethyl hydrazino group) of the carbon numbers 1-6. the carbon numbers 1-15 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- an ureido group (for example an ureido group.) of the carbon numbers 1-6 a NN-dimethyl ureido group and the carbon numbers 1-15 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- an imido group (for example succinimide group) of the carbon numbers 1-6. the carbon numbers 1-20 -- desirable -- the carbon numbers 1-12 -- further -- desirable -- an alkylthio group (for example methylthio.) of the carbon numbers 1-8 ethylthio propylthio and the carbon numbers 6-20 -- desirable -- the carbon numbers 6-12 -- further -- desirable -- an arylthio group (for example chloro phenylthio phenylthio-methyl phenylthio) of the carbon numbers 6-10 2-pyridylthio naphthyl thio and the carbon numbers 2-20 -- desirable -- the carbon numbers 2-12 -- further -- desirable -- an alkoxycarbonyl group (for example carbomethoxy.) of the carbon numbers 2-8 ethoxycarbonyl 2-benzyloxycarbonyl and the carbon numbers 6-20 -- desirable -- the carbon numbers 6-12 -- further -- desirable -- an aryloxy carbonyl group (for example phenoxycarbonyl) of the carbon numbers 6-10 [0037] the carbon numbers 1-18 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- a non-substituted alkyl group (for example methyl.) of the carbon numbers 1-5 ethyl propyl butyl and the carbon numbers 1-18 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- a substituted alkyl group of the carbon numbers 1-5 -- { -- for example hydroxymethyl. Trifluoromethyl benzyl carboxy ethyl ethoxy carbonyl methyl acetyl aminomethyl

and here -- the carbon numbers 2-18 -- desirable -- the carbon numbers 3-10 -- further -- desirable -- an unsaturated hydrocarbon group (for example a vinyl group.) of the carbon numbers 3-5 An ethynyl group 1-cyclohexenyl group a benzyldiyne group and a benzyliene group will also be contained in a substituted alkyl group} the carbon numbers 6-20 -- desirable -- the carbon numbers 6-15 -- further -- desirable -- an aryl group (for example phenyl.) which is not replaced [ substitution of the carbon numbers 6-10 or ] Naphthylp-carboxyphenylp-nitrophenyl 3,5-dichlorophenylp-cyanophenylm-fluorophenylp-tolyl [0038] the carbon numbers 1-20 -- desirable -- the carbon numbers 2-10 -- a heterocycle group (for example pyridyl 5-methyl pyridyl thienyl a furil morpholinotetrahydrofurfuryl) which is not replaced [ substitution of the carbon numbers 4-6 or ] is mentioned still more preferably. Structure which the benzene ring and a naphthalene ring condensed can also be taken. V may replace further on these substituents. Things desirable as a substituent are an above-mentioned alkyl group an aryl group an alkoxy group a halogen atom and benzene ring condensation and are a methyl group a phenyl group a methoxy group chlorine atom a bromine atom iodine atom and benzene ring condensation still more preferably. [0039] Although a halogen atom an alkyl group an aryl group a heterocycle group a carboxyl group a phosphate group etc. are mentioned preferably as the substituent V on  $Z_1Z_2Z_3Z_4Z_5$  and  $Z_6$  A phenyl group a naphthyl group a biphenyl group a thienyl group a furil group a carboxyl group and a phosphate group are still more preferred also in an aryl group a heterocycle group a carboxyl group and a phosphate group and even if these are replaced further they are more preferably preferred. Especially it is phenyl preferably and a carboxyl group and a phosphate group may replace. [0040] General formula (I) and  $R_1$  in general formula (IV)  $R_3$  A substituent etc. which expressed an aryl group which is not replaced [ an alkyl group which is not replaced / substitution or / substitution or ] and were shown by explanation of the substituent V etc. as a substituent are mentioned and  $R_4$  expresses an alkyl group preferably replaced by an aryl group an aryl group or a heterocycle group which is not replaced [ substitution or ]. And coloring matter in general formula (I) and general formula (IV) must turn into cation coloring matter. therefore -- as the alkyl group expressed with  $R_1R_3$  and  $R_4$  -- for example the carbon numbers 1-18 -- desirable -- 1 to 7 -- as for 1 to 4 a non-substituted alkyl group preferably especially. for example methyl ethyl propyl isopropyl butyl and isobutyl. Hexyloctyldodecyloctadecylan unsaturated hydrocarbon group. (for example allyl and a clo chill) and a hydroxyalkyl group (for example 2-

hydroxyethyl.) 3-hydroxypropyl and an alkoxyalkyl group (for example 2-methoxy ethyl.) 2-(2-methoxyethoxy) ethyl an alkoxy carbonyl-alkyl group. (For example ethoxy carbonyl ethyl 2-benzyloxy carbonyl ethyl) An acyloxy alkyl group (for example 2-acetyloxy ethyl) an acyl alkyl group (2-acetyl ethyl) As a carbamoyl alkyl group (for example 2-morpholino carbonyl ethyl) a sulfamoyl alkyl group (for example NN-dimethyl sulfamoyl methyl) and an alkyl group that an aryl group replaced An aralkyl group (for example benzyl 2-phenylethyl naphthyl methyl 2-(4-biphenyl) ethyl) an aryloxy alkyl group (for example 2-phenoxyethyl and 2-(1-naphthoxy) ethyl.) 2-(4-BIFENIROKISHI) ethyl 2-(omp-halo phenoxy) ethyl 2-(omp-methoxy phenoxy) ethyl an aryloxy carbonyl alkyl group (3-phenoxy carbonyl propyl 2-(1-naphthoxy carbonyl) ethyl) etc. are mentioned. For example 2-(pyrrolidine 2-\*\*\*\*-1-yl) ethyl 2-(2-pyridyl) ethyl 2-(4-pyridyl) ethyl 2-(2-furyl) ethyl 2-(2-thienyl) ethyl and 2-(2-pyridyl methoxy) ethyl are mentioned as a heterocyclic substituted alkyl group.

Phenyl naphthyl biphenyl etc. are mentioned as an aryl group expressed with  $R_1$ ,  $R_3$  and  $R_4$ .

[0041] Although it is the alkyl group replaced by an aryl group an aryl group or a heterocycle group which is not replaced [above-mentioned substitution desirable as a substituent expressed with  $R_1$ ,  $R_3$  and  $R_4$  or ] What is replaced with an ammonio group which has cation electric charge such as a trialkyl ammonio group further has these more preferred. As a desirable ammonio group an unreplaced trialkyl ammonio group of the carbon numbers 1-7. for example a trimethylammonio group a triethylammonio group and a TORIPURO pill ammonio group. What is expressed with the above-mentioned V as a tributylammonio group a dimethylethyl ammonio group a dibutylethylammonio group and a substitution trialkyl ammonio group (substituent of the carbon numbers 1-7 is mentioned. For example a trichloromethyl ammonio group a Tori (2-methoxy) ethyl ammonio group A Tori (33-dichloropropyl) ammonio group a dibutyl (2-hydroxyethyl) ammonio group The 4th class of nitrogen-containing heterocyclic nitrogen salt (for example 1-pyridinio group a 1-methyl-4-pyridinio group 1-kino RINIO group and 3-thia ZORINIO group may be mentioned and these may be replaced by the further above-mentioned substituent V etc.) of the carbon numbers 1-18 etc. are mentioned. A desirable ammonio group an unreplaced trialkyl ammonio group of the carbon numbers 1-4. It is (for example a trimethylammonio group a triethylammonio group a TORIPURO pill ammonio group and a tributylammonio group) and 1-pyridinio group and they are a trimethylammonio group a triethylammonio group and 1-pyridinio group especially preferably.

[0042] A substituent etc. which  $R_2$ ,  $R_5$  and  $R_6$  expressed an alkyl group or an

aryl group and were shown by explanation of the substituent V etc. as a substituent are mentioned among general formula (II) and general formula (V). An alkyl group preferably replaced by an aryl group or an aryl group or a heterocycle group which is not replaced [ substitution or ] is expressed. And coloring matter in general formula (II) and general formula (V) must turn into anion coloring matter. therefore -- as the alkyl group expressed with  $R_2R_5$  and  $R_6$  -- for example the carbon numbers 1-15 -- desirable -- the carbon numbers 1-10 -- especially -- desirable -- an alkyl group of the carbon numbers 1-5 -- a sulfonic group. what a phosphate group and/or a carboxyl group replaced (for example sulfo-methyl.) Sulfoethyl 2,2-difluoro-2-carboxyethyl a 2-phospho ethyl group An unsaturated hydrocarbon group which a sulfonic group a phosphate group and/or a carboxyl group replaced. (For example 3-sulfo- 2-propenyl) a sulfonic group a phosphate group And/or an alkoxyalkyl group which a carboxyl group replaced. An alkoxycarbonyl-alkyl group which (for example 2-sulfo- methoxy ethyl) a sulfonic group a phosphate group and/or a carboxyl group replaced. (For example sulfo-ethoxycarbonyl ethyl 2-sulfo-benzoyloxy carbonyl ethyl) An acyloxy alkyl group (for example 2-phospho acetyloxy ethyl) and an acyl alkyl group (2-sulfo-acetyl ethyl) which a sulfonic group a phosphate group and/or a carboxyl group replaced are mentioned. An aryl group as a replaced alkyl group A sulfonic group a phosphate group and/or an aralkyl group (for example 2-sulfo benzyl.) which a carboxyl group replaced 4-sulfo benzyl 4-sulfo phenethyl 3-phenyl-3-sulfo propyl 3-phenyl-2-sulfo propyl 4,4-diphenyl-3-sulfo-butyl 2-(4'-sulfo-4-biphenyl) ethyl 4-phospho benzyl A sulfonic group a phosphate group and/or an aryloxy carbonyl alkyl group that a carboxyl group replaced (3-sulfo-phenoxy carbonyl propyl) An aryloxy alkyl group (for example 2-(4-sulfo-phenoxy) ethyl 2-(2-phospho phenoxy) ethyl 4,4-diphenoxy-3-sulfo-butyl) etc. which a sulfonic group a phosphate group and/or a carboxyl group replaced are mentioned. As an alkyl group replaced by a heterocycle group 3-(2-pyridyl)-3-sulfo propyl 3-(2-furyl)-3-sulfo propyl 2-(2-thienyl)-2-sulfo propyl etc. are mentioned.

[0043]  $R_2R_5$  and an above-mentioned sulfonic group desirable as a substituent expressed with  $R_6$  An aralkyl group a sulfonic group which a phosphate group and/or a carboxyl group replaced An unsaturated hydrocarbon group a sulfonic group which a phosphate group and/or a carboxyl group replaced It is the aryloxy alkyl group which a phosphate group and/or a carboxyl group replaced More preferably 2-sulfo benzyl 4-sulfo benzyl 4-sulfo phenethyl 3-phenyl-3-sulfo propyl 3-phenyl-2-sulfo propyl They are 4,4-diphenyl-3-sulfo-butyl 2-(4'-sulfo- 4-biphenyl) ethyl 4-phospho benzyl 3-sulfo- 2-propenyl 2-(4-sulfo-phenoxy) ethyl etc.

[0044]  $L_1, L_2, L_3, L_4, L_5, L_6, L_7, L_8, L_9, L_{10}, L_{11}, L_{12}, L_{13}, L_{14}, L_{15}, L_{16}, L_{17}$  and  $L_{18}$  express a methine group independently respectively. A methine group expressed with  $L_1 - L_{18}$  may have a substituent as a substituent -- for example the carbon numbers 1-15 which are not replaced [ substitution or ] -- desirable -- the carbon numbers 1-10 -- especially -- desirable -- an alkyl group of the carbon numbers 1-5. the carbon numbers 6-20 which are not replaced [ (for example methyl ethyl and 2-carboxyethyl) substitution or ] -- desirable -- the carbon numbers 6-15 -- further -- desirable -- an aryl group (for example phenyl.) of the carbon numbers 6-10 the carbon numbers 3-20 which are not replaced [ o-carboxyphenyl substitution or ] -- desirable -- the carbon numbers 4-15 -- further -- desirable -- a heterocycle group (for example NN-dimethylbarbituric acid group) of the carbon numbers 6-10. a halogen atom (for example chlorine bromine iodine fluoride) and the carbon numbers 1-15 -- desirable -- the carbon numbers 1-10 -- further -- desirable -- an alkoxy group (for example methoxy.) of the carbon numbers 1-5 ethoxy and the carbon numbers 0-15 -- desirable -- the carbon numbers 2-10 -- further -- desirable -- an amino group (for example methylamino NN-dimethylamino N-methyl-N-phenylamino N-methyl piperazino) of the carbon numbers 4-10 and the carbon numbers 1-15 -- desirable -- the carbon numbers 1-10. furthermore -- desirable -- an alkylthio group (for example methylthio ethylthio) of the carbon numbers 1-5 and the carbon numbers 6-20 -- desirable -- the carbon numbers 6-12 -- an arylthio group (for example phenylthio p-methyl phenylthio) of the carbon numbers 6-10 etc. are mentioned still more preferably. Other methine groups and rings may be formed or an auxochrome ring can also be formed.

[0045]  $p_1, p_2, p_3, p_4, p_5$  and  $p_6$  express 0, 1 or 2 or 3 independently respectively. It is 0, 1 and 2 preferably and is 0 and 1 still more preferably. When  $p_1, p_2, p_3, p_4, p_5$  and  $p_6$  are two or more it does not need to be the same although a methine group is repeated.

[0046]  $n_1$  and  $n_2$  express 0 or 1 independently respectively. It is 0 preferably.

[0047] When required in order to make ionic charge of a molecule into neutrality  $M_1, M_2, M_3$  and  $M_4$  are contained in a formula in order to show existence of a positive ion or negative ion. as a typical positive ion -- a hydrogen ion ( $H^+$ ) and alkali metal ion (sodium ion.) Inorganic ions such as potassium ion, a lithium ion and alkaline earth metal ion (for example calcium ion) Organic ions such as ammonium ion (for example ammonium ion, tetra alkyl ammonium ion, pyridinium ion, ethylpyridinium ion) is mentioned. negative ion may be any of inorganic anions or organic negative ion -- halogen negative ion (for example a fluorine ion.) a chloride ion, a



bromine ion iodine ion and substitution aryl sulfone acid ion (for example p-toluenesulfonic acid ion.) p-chlorobenzenesulfonic acid ion and aryl disulfon acid ion (for example 1,3-benzenedisulfonic acid ion.) 15-naphthalene disulfon acid ion 2,6-naphthalene disulfon acid ion Alkyl-sulfuric-acid ion (for example methylsulfuric acid ion) sulfate ion thiocyanic acid ion a perchlorate ion tetrafluoroboric acid ion picric acid ion acetate ion and trifluoromethanesulfonic acid ion are mentioned. Furthermore ionicity polymer or a molecule and a molecule that has reverse charge may be used.  $m_1, m_2, m_3$  and  $m_4$  are 0 when a number required to balance an electric charge is expressed and it forms a salt by intramolecular.

[0048] the number of methine groups in  $Q_1$  or  $Q_2$  -- desirable -- 0 to 7 -- further -- desirable -- 0 to 5 -- it is 3 especially preferably. It is preferred that a substituent (a heterocycle group an aliphatic group or an aromatic group) required to form methine coloring matter in a methine group replaces a heterocycle group or an aromatic group is mentioned as a desirable substituent and it is a heterocycle group especially preferably. What was mentioned as an example of the above-mentioned  $Z_4$  and  $Z_6$  as a heterocycle group is preferred. As an aromatic group an aromatic group (for example 4-dimethylaminophenyl group 4-methoxyphenyl group a phenyl group 4-dimethylamino naphthyl group) etc. which is not replaced [ substitution or ] are mentioned. As an aliphatic group an alkoxy carbonyl group (for example ethoxy carbonyl group) and an acyl group (for example acetyl group) are preferred. They are mentioned by substituent etc. which were shown by the above-mentioned V and In addition for example an amino group which is not replaced [ substitution or ]. An acyl group (for example acetyl group) which is not replaced [ an alkyl sulfonyl group (for example methylsulfonyl group) which is not replaced / (for example an amino group and a dimethylamino group) a cyano group an alkoxy carbonyl group (for example ethoxy carbonyl) substitution or /substitution or ] is preferred.

[0049] Although an example of a compound expressed with } which contains general formula (IV) of a general formula (I) {subordinate concept of this invention in below is shown this invention is not limited to these.

[0050]

[Formula 12]

[0051]

[Formula 13]

[0052]  
[Formula 14]

[0053]  
[Formula 15]

[0054]  
[Formula 16]

[0055]  
[Formula 17]

[0056]  
[Formula 18]

[0057]  
[Formula 19]

[0058]  
[Formula 20]

[0059]  
[Formula 21]

[0060]  
[Formula 22]

[0061]  
[Formula 23]

[0062]

[Formula 24]

[0063]

[Formula 25]

[0064]

[Formula 26]

[0065]

[Formula 27]

[0066]

[Formula 28]

[0067]

[Formula 29]

[0068]

[Formula 30]

[0069]

[Formula 31]

[0070]

[Formula 32]

[0071]

[Formula 33]

[0072]

[Formula 34]

[0073]  
[Formula 35]

[0074]  
[Formula 36]

[0075]  
[Formula 37]

[0076]  
[Formula 38]

[0077]  
[Formula 39]

[0078]  
[Formula 40]

[0079]  
[Formula 41]

[0080]  
[Formula 42]

[0081] Although the example of a compound expressed with } which contains  
general formula (V) of the general formula (II) {subordinate concept of  
this invention in below is shown this invention is not limited to these.

[0082]  
[Formula 43]

[0083]  
[Formula 44]

[0084]  
[Formula 45]

[0085]  
[Formula 46]

[0086]  
[Formula 47]

[0087]  
[Formula 48]

[0088]  
[Formula 49]

[0089]  
[Formula 50]

[0090]  
[Formula 51]

[0091]  
[Formula 52]

[0092]  
[Formula 53]

[0093]

[Formula 54]

[0094]  
[Formula 55]

[0095]  
[Formula 56]

[0096]  
[Formula 57]

[0097]  
[Formula 58]

[0098]  
[Formula 59]

[0099]  
[Formula 60]

[0100]  
[Formula 61]

[0101]  
[Formula 62]

[0102]  
[Formula 63]

[0103]  
[Formula 64]

[0104]  
[Formula 65]

[0105]  
[Formula 66]

[0106]  
[Formula 67]

[0107]  
[Formula 68]

[0108]  
[Formula 69]

[0109]  
[Formula 70]

[0110]  
[Formula 71]

[0111]  
[Formula 72]

[0112]  
[Formula 73]

[0113] Next the compound expressed with general formula (III) is described in detail. D expresses a sensitizing dye portion with the adsorptivity to semiconductor particulates such as a titanium dioxide among general

formula (III). As coloring matter of Dcyanine dyemerocyanine dyeoxonol dyeJolo Pau Ra cyanine dyea hemicyanine dyestyryl system coloring matterhemi oxonol dyea xanthene dye and doria -- metal chelate compound of reel methane series coloring mattera thiazine pigmentan acridine dyean oxazine pigmentaminonaphthalene system coloring matterphthalocyanine system coloring matterporphyrin system coloring matterand othersetc. are contained. Cyanine dyemerocyanine dyerhoda cyanine dye3 core merocyanine dyeAROPORA coloring mattera hemicyanine dyea styryl pigmentetc. are mentioned preferably. Under the present circumstancesthe substituent on the methine chain which forms coloring matter also contains in cyanine dye the thing in which the SUKUARIUMU ring and the crocodile NIUMU ring were formed. About the details of these coloring matter. F.M Harmer (F. M. Harmer) work "heterocyclic party UNZU Cyanine Dyes and Related Compounds (Heterocyclic Compounds-Cyanine Dyes.) and Related Compounds" John Willie and Sons (John Wiley & Sons)- New YorkLondon1964 annual publicationsDay em Sturmer (D. M. Sturmer) work "heterocyclic Compounds-Special topics in heterocyclic chemistry (Heterocyclic Compounds-Special.) It is indicated to topics in heterocyclic chemistry"Chapter 18Section 14and the 482nd to 515 pages etc. As for the general formula of cyanine dyemerocyanine dyeand rhoda cyanine dyewhat is shown in U.S. Pat. No. 5340694 21st22-page (XI) (XII)and (XIII) is preferred. As for Dit is preferred to have an adsorbent high substituent to semiconductor particulatesuch as a titanium dioxide. You may make it adsorb by any of physical adsorption or chemical absorption. Although a carboxyl groupa phosphate groupa sulfonic groupa sulfinic acid grouphydroxylan amino groupor a sulfhydryl group is mentioned as a typical adsorptivity substituentthey are a carboxyl group and a phosphate group more preferably.

[0114]As an example of representation of luminescent coloring matter shown by Acyanine dyemerocyanine dyeOxonol dyeJolo Pau Ra cyanine dyea hemicyanine dyestyryl system coloring matterhemi oxonol dyea xanthene dyeand doria -- metal chelate compound of reel methane series coloring mattera thiazine pigmentan acridine dyean oxazine pigmentaminonaphthalene system coloring matterphthalocyanine system coloring matterporphyrin system coloring matterand othersetc. are contained. A thing with skeletal structure of coloring matter used for dye laser as a kind of these luminescent coloring matter is preferred. These are arranged in for exampleMitsuo Maedalaser researchthe 8th volume694 pages803 pages958 pages (1980) and the 9th volume85 pages (1981) and F. Sehaefer workDye Lasersand Springer (1973). Cyanine dyemerocyanine dyerhoda cyanine dye3 core merocyanine dyeAROPORA



coloring matter hemicyanine dyes styryl pigments etc. are mentioned more preferably.

[0115] L expresses a divalent connecting group or a single bond. This connecting group consists of an atom or an atom group who contains at least one sort in a carbon atom a nitrogen atom a sulfur atom and an oxygen atom preferably. desirable -- an alkylene group (for example methylene ethylene propylene butylene pentylene) an allylene group (for example phenylene naphthylene) and an alkenylene group (for example) -- for example ethenylene propenylene and alkynylene group (for example ethynylene.) Propynylene an amide group an ester group a sulfo amide group a sulfonic ester group An ureido group a sulfonyl group a sulfinyl group a thioether group an ether group the Alko Nils group and  $-N(Ra)-$  (Ra -- an alkyl group which is not replaced [ a hydrogen atom substitution or ].) an aryl group which is not replaced [ substitution or ] is expressed -- a heterocyclic divalent group (for example a 6-chloro-1,3,5-triazine 2,4-diyl group.) A with an or more 1 carbon number [ or less 20 ] constituted combining a pyrimidine 2,4-diyl group and a quinoxaline 2,3-diyl group one or more than it divalent connecting group is expressed. furthermore -- desirable -- a with a carbon number of four or less alkylene group (for example methylene and ethylene.) propylene butylene a with an or more 6 carbon number [ or less 10 ] allylene group (for example phenylene naphthylene) and a with a carbon number of four or less alkenylene group (for example) -- for example It is a divalent connecting group or a single bond with an or more 1 carbon number [ or less 10 ] constituted combining ethenylene propenylene with a carbon number of four or less alkynylene group (for example ethynylene propynylene) an amide group an ester group a sulfo amide group and a sulfonic ester group one or more than it.

[0116] n may be one or more integers and two or more L and A in which a case of two or more is included may be different connecting groups and luminescent coloring matter portions respectively.

[0117]  $Z_7Z_8Z_9Z_{10}Z_{11}Z_{12}$  and  $Z_{13}$  express an atomic group required to form nitrogen-containing heterocycle among general formula (VI) general formula (VII) and general formula (VIII). As nitrogen-containing heterocycle formed of  $Z_7Z_8Z_9Z_{11}$  and  $Z_{13}$  a thiazoline core a thiazole core a benzothiazole core an oxazoline core an oxazole core a benzoxazole core a selenazoline core a selenazole core a benzoselenazole core a 3,3'-dialkyl INDO core (for example 3,3'-dimethyl INDO core) an imidazoline core an imidazole core a benzimidazole core 2-pyridine core 4-pyridine core 2-quinoline core 4-quinoline core 1-isoquinoline core 3-isoquinoline core imidazo [4,5-b] Although a quinoxaline core an oxadiazole core a

thiadiazole corea tetrazole corea pyrimidine base etc. can be mentioned Preferably A benzothiazole corea benzoxazol corea 3,3-dialkyl INDO renin core (for example 3,3-dimethyl INDO renin) A benzimidazole core 2-pyridine core 4-pyridine core 2-quinoline core It is 4-quinoline core 1-isoquinoline core and 3-isoquinoline core and they are a benzothiazole corea benzoxazol corea 3,3-dialkyl INDO renin core (for example 3,3-dimethyl INDO renin) and a benzimidazole core still more preferably.

[0118] The same example as a case on said  $Z_1 - Z_6$  is given. V may replace further on these substituents. Things desirable as a substituent are an above-mentioned alkyl group an aryl group an alkoxy group a halogen atom and benzene ring condensation and are a methyl group a phenyl group a methoxy group chlorine atom a bromine atom an iodine atom and benzene ring condensation still more preferably.

[0119] When methine coloring matter expressed with general formula (VI) (VII) or (VIII) expresses an adsorptivity sensitizing dye portion expressed with D in general formula (I) Preferably as the substituent V on  $Z_7Z_8Z_9Z_{11}$  and  $Z_{13}$  A halogen atom Although an alkyl group an aryl group a heterocycle group a carboxyl group a phosphate group a hydroxyl group an amino group a sulfonic group or a sulfhydryl group is mentioned More preferably An aryl group a heterocycle group a carboxyl group a phosphate group It is especially preferred a phenyl group a naphthyl group a biphenyl group a thienyl group a furil group \*\* and also that it is desirable and these are further replaced by a carboxyl group a phosphate group a hydroxyl group an amino group a sulfonic group or a sulfhydryl group. It is preferably by carboxyl group a phosphate group a hydroxyl group an amino group a sulfonic group or a sulfhydryl group and they are a carboxyl group and a phosphate group especially preferably.

[0120] When methine coloring matter expressed with general formula (VI) (VII) or (VIII) expresses a luminescent coloring matter portion expressed with A in general formula (I) Although a halogen atom an alkyl group an aryl group a heterocycle group etc. are mentioned preferably as the substituent V on  $Z_7Z_8Z_9Z_{11}$  and  $Z_{13}$  more -- desirable -- an aryl group a heterocycle group and inside -- a phenyl group a naphthyl group a biphenyl group a thienyl group a furil group and \*\* -- they are chlorobromomethyl ethyl phenyl thienyl and a furil desirable especially preferably.

[0121] General formula (VI) general formula (VII) and general formula (VIII) Inner  $R_7$  A substituent etc. which  $R_8R_9R_{11}$  and  $R_{13}$  expressed an aryl group which is not replaced [ an alkyl group which is not replaced / substitution or / substitution or ] and were shown by explanation of the

substituent V etc. as a substituent are mentioned. as an alkyl group -- for example the carbon numbers 1-18 -- desirable -- 1 to 7 -- as for 1 to 4 a non-substituted alkyl group preferably especially. for example methyl ethyl propyl isopropyl butyl and isobutyl.

Hexyloctyldodecyloctadecylan aralkyl group. (For example benzyl 2-phenylethyl naphthyl methyl 2-(4-biphenyl) ethyl) An unsaturated hydrocarbon group (for example allyl cyclohexyl) a hydroxyalkyl group. (For example 2-hydroxyethyl and 3-hydroxypropyl) an alkoxyalkyl group. (For example 2-methoxy ethyl 2-(2-methoxyethoxy) ethyl) an aryloxy alkyl group (for example 2-phenoxyethyl and 2-(1-naphthoxy) ethyl.) 2-(4-BIFENIROKISHI) ethyl 2-(ortho-halo phenoxy) ethyl 2-(ortho-methoxy phenoxy) ethyl an alkoxy carbonyl-alkyl group. (For example ethoxy carbonyl ethyl and 2-benzyloxy carbonyl ethyl) an aryloxy carbonyl alkyl group (3-phenoxy carbonyl propyl 2-(1-naphthoxy carbonyl) ethyl) an acyloxy alkyl group (for example) 2-acetyloxy ethyl an acyl alkyl group (2-acetyl ethyl) A carbamoyl alkyl group (for example 2-morpholino carbonyl ethyl) a sulfamoyl alkyl group (for example NN-dimethyl sulfamoyl methyl) a heterocyclic substituted alkyl group (for example 2-(pyrrolidine 2-\*\*\*\*-1-yl) ethyl) etc. are mentioned. Phenyl naphthyl biphenyl furil thienyl etc. are mentioned as an aryl group expressed with  $R_1$ ,  $R_3$  and  $R_4$ .

[0122] When methine coloring matter expressed with general formula (VI) (VII) or (VIII) expresses an adsorptivity sensitizing dye portion expressed with D in general formula (I) as the substituent expressed with  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{13}$  -- desirable -- a substituted alkyl group (as a substituent -- a carboxyl group.) Although an aralkyl group an aryloxy alkyl group a carboxy alkyl group a sulfoalkyl group etc. with which a phosphate group hydroxylan amino group a sulfonic group or a sulfhydryl group is mentioned are mentioned It is preferred that these are further replaced by a carboxyl group a phosphate group hydroxylan amino group a sulfonic group or sulfhydryl group. They are a carboxyl group a phosphate group and the alkyl group replaced as be alike preferably.

[0123] When methine coloring matter expressed with general formula (VI) (VII) or (VIII) expresses a luminescent coloring matter portion expressed with A in general formula (I)  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and an above-mentioned non-substituted alkyl group desirable as a substituent expressed with  $R_{13}$  It is an aralkyl group an aryloxy alkyl group a carboxy alkyl group and a sulfoalkyl group and they are a non-substituted alkyl group an aralkyl group and a sulfoalkyl group still more preferably.

[0124] Although  $Z_{10}$  expresses an atomic group required to form an acidic nucleosa form of an acidic nucleus of what kind of common merocyanine dye can also be taken. With an acidic nucleus said herefor example The

4th edition of James (James) editing "the theory OBU the photographic process" (The Theory of the Photographic Process) 198 pages will define in the Macmillan publishing company and 1977. Specifically what is indicated to U.S. Pat. No. 3567719 No. 3575869 No. 3804634 No. 3837862 No. 4002480 No. 4925777 JP3-167546A etc. is mentioned. When an acidic nucleus forms a nitrogen-containing heterocyclic compound of 5 members or six membered-rings which consists of carbon nitrogen and a chalcogen (typically oxygen sulfur selenium and tellurium) atom it is preferred and the following core is mentioned. 2-pyrazolone 5-one pyrazolidine 35-dione imidazoline 5-one Hydantoin 2 or 4-thiohydantoin 2-imino oxazolidine 4-one 2-oxazoline 5-one 2-thiooxazolin-24-dione Isooxazoline 5-one 2-thiazoline 4-one thiazolidine 4-one Thiazolidine 24-dione rhodaninethiazolidine 24-dithione Isorhodanine Indang 13-dione thiophene 3-one thiophene 3-\*\*\*\*- 11-dioxide indoline 2-one indoline 3-one 2-oxo inda ZORIUMU 3-oxo inda ZORIUMU the 57-dioxo 67-dihydro CHIAZORO [32-a] Pyrimidine cyclohexane-13-dione 34-dihydro isoquinoline 4-one 13-dioxane-46-dione barbituric acid 2-thio BARUNI tool acid coumarin 24-dione indazoline-2-one pyrid [12-a] Pyrimidine 13-dione pyrazolo [15-b] Chinae-cortex ZORONPIROZORO [15-a] Benzimidazole pyrazolo pyridone 1234-tetrahydroquinoline 24-dione the 3-oxo 23-JIHIDOROBENZO [d] Thiophene 11-dioxide 3-dicyano methine 23-JIHIDOROBENZO [d] A core of the thiophene 1 and 1-dioxide.

[0125] Preferably as  $Z_{10}$  Hydantoin 2 or 4-thiohydantoin 2-oxazoline 5-one 2-thiooxazolin-24-dione Thiazolidine 24-dione rhodaninethiazolidine 24-dithione It is barbituric acid and 2-thio BARUNI tool acid and they are hydantoin 2 or 4-thiohydantoin 2-oxazoline 5-one rhodanine barbituric acid and 2-thio BARUNI tool acid still more preferably. It is 4-thiohydantoin and 2-oxazoline 5-one especially preferably.

[0126] Nitrogen-containing heterocycle of 5 members or 6 members formed of  $Z_{12}$  removes an oxo group or a thio oxo group from heterocycle expressed by  $Z_{10}$ . Preferably Hydantoin 2 or 4-thiohydantoin 2-oxazoline 5-one 2-thiooxazolin-24-dione thiazolidine 24-dione From rhodaninethiazolidine 24-dithione barbituric acid and 2-thio BARUNI tool acid to an oxo group. Or except for a thio oxo group an oxo group or a thio oxo group is removed from hydantoin 2 or 4-thiohydantoin 2-oxazoline 5-one rhodanine barbituric acid and 2-thio BARUNI tool acid still more preferably. An oxo group or a thio oxo group is especially removed from 4-thiohydantoin 2-oxazoline 5-one and rhodanine preferably.

[0127] As an alkyl group expressed as  $R_{10}$  and  $R_{12}$  a non-substituted alkyl group quoted as example such as above-mentioned  $R_1$  or a substituted alkyl group is mentioned and same thing is preferred. the carbon numbers 2-20 -

- desirable -- the carbon numbers 6-10 -- further -- desirable -- an  
 unreplaced aryl group (for example a phenyl group.) of the carbon numbers  
 6-8 1-naphthyl group and the carbon numbers 2-20 -- desirable -- the  
 carbon numbers 6-10 -- further -- desirable -- a substitution aryl group  
 (for example an aryl group which V quoted as substituentssuch as the  
 above-mentioned Z<sub>1</sub>replaced is mentioned.) of the carbon numbers 6-8  
 specifically p-methoxyphenyl group p-methylphenyl group p-chlorophenyl  
 group etc. are mentioned. the carbon numbers 1-20 -- desirable -- the  
 carbon numbers 3-10 -- further -- desirable -- an unreplaced heterocycle  
 group (for example 2-furyl group.) of the carbon numbers 4-8 A 2-thienyl  
 group 2-pyridyl group 3-pyrazolyl group isoxazolyl 3-isothiazolyl 2-  
 imidazolyl 2-oxazolyl 2-thiazolyl 2-pyridazolyl 3-pyrazolyl 2- (1,3,5-  
 triazolyl) 5-tetra ZORIRU and the carbon numbers 1-20 -- desirable -- the  
 carbon numbers 3-10 -- further -- desirable -- a substitution  
 heterocycle group (for example an aryl group which V quoted as  
 substituentssuch as the above-mentioned Z<sub>1</sub>replaced is mentioned.) of the  
 carbon numbers 4-8 Specifically a 5-methyl-2-thienyl group a 4-methoxy-2-  
 pyridyl group etc. are mentioned. It is mentioned. A desirable thing as  
 R<sub>10</sub> and R<sub>12</sub> Methyl ethyl It is 2-sulfoethyl 3-sulfopropyl 3-sulfobutyl 4-  
 sulfobutyl carboxymethyl phenyl 2-pyridyl and 2-thiazolyl and they are  
 ethyl 2-sulfoethyl carboxymethyl phenyl and 2-pyridyl still more preferably.  
 [0128] L<sub>19</sub>L<sub>20</sub>L<sub>21</sub>L<sub>22</sub>L<sub>23</sub>L<sub>24</sub>L<sub>25</sub>L<sub>26</sub>L<sub>27</sub>L<sub>28</sub>L<sub>29</sub>L<sub>30</sub>L<sub>31</sub>L<sub>32</sub>L<sub>33</sub>L<sub>34</sub>L<sub>35</sub>L<sub>36</sub>L<sub>37</sub> and L<sub>38</sub> express a methine  
 group independently respectively. A methine group expressed with L<sub>19</sub> - L<sub>38</sub>  
 may have a substituent as a substituent -- for example the carbon numbers  
 1-15 which are not replaced [ substitution or ] -- desirable -- the  
 carbon numbers 1-10 -- especially -- desirable -- an alkyl group of the  
 carbon numbers 1-5. the carbon numbers 6-20 which are not replaced  
 [ (for example methyl ethyl and 2-carboxyethyl) substitution or ] --  
 desirable -- the carbon numbers 6-15 -- further -- desirable -- an aryl  
 group (for example phenyl.) of the carbon numbers 6-10 the carbon numbers  
 3-20 which are not replaced [ o-carboxyphenyl substitution or ] --  
 desirable -- the carbon numbers 4-15 -- further -- desirable -- a  
 heterocycle group (for example NN-dimethylbarbituric acid group) of the  
 carbon numbers 6-10. a halogen atom (for  
 example chlorine bromine iodine fluoride) and the carbon numbers 1-15 --  
 desirable -- the carbon numbers 1-10 -- further -- desirable -- an  
 alkoxy group (for example methoxy.) of the carbon numbers 1-5 ethoxy and  
 the carbon numbers 0-15 -- desirable -- the carbon numbers 2-10 --  
 further -- desirable -- an amino group (for example methylamino NN-  
 dimethylamino N-methyl-N-phenylamino N-methyl piperazino) of the carbon  
 numbers 4-10 and the carbon numbers 1-15 -- desirable -- the carbon

numbers 1-10. furthermore -- desirable -- an alkylthio group (for example methylthioethylthio) of the carbon numbers 1-5 and the carbon numbers 6-20 -- desirable -- the carbon numbers 6-12 -- an arylthio group (for example phenylthio-methyl phenylthio) of the carbon numbers 6-10 etc. are mentioned still more preferably. Other methine groups and rings may be formed or an auxochrome ring can also be formed.

[0129]  $n_3, n_4, n_5$  and  $n_6$  express 0 or 1 independently respectively. It is 0 and 2 preferably and is 0 and 1 still more preferably. When  $n_3, n_4, n_5$  and  $n_6$  are two or more it does not need to be the same although a methine group is repeated.

[0130]  $p_7, p_8, p_9, p_{10}$  and  $p_{11}$  express 0 or 1 independently respectively. It is 0 preferably.

[0131] When required in order to make ionic charge of a molecule into neutrality  $M_5, M_6$  and  $M_7$  are contained in a formula in order to show existence of a positive ion or negative ion. as a typical positive ion -- a hydrogen ion ( $H^+$ ) and alkali metal ion (sodium ion.) Inorganic ions such as potassium ion, a lithium ion and alkaline earth metal ion (for example calcium ion) Organic ions such as ammonium ion (for example ammonium ion, tetra alkyl ammonium ion, pyridinium ion, ethylpyridinium ion) is mentioned. negative ion may be any of inorganic anions or organic negative ion -- halogen negative ion (for example a fluorine ion.) a chloride ion, a bromine ion, an iodine ion and substitution aryl sulfone acid ion (for example p-toluenesulfonic acid ion.) p-chlorobenzenesulfonic acid ion and aryl disulfon acid ion (for example 1,3-benzenedisulfonic acid ion.) 1,5-naphthalene disulfon acid ion, 2,6-naphthalene disulfon acid ion, Alkyl-sulfuric acid ion (for example methylsulfuric acid ion), sulfate ion, thiocyanic acid ion, a perchlorate ion, tetrafluoroboric acid ion, picric acid ion, acetate ion and trifluoromethanesulfonic acid ion are mentioned. Furthermore ionicity polymer or a molecule and a molecule that has reverse charge may be used.  $m_5, m_6$  and  $m_7$  are 0 when a number required to balance an electric charge is expressed and it forms a salt by intramolecular.

[0132] It is general formula (III) of this invention below. Although an example of a compound expressed with [general formula (VI) of a subordinate concept (VII) and (VIII) are included] is shown this invention is not limited to these.

[0133]

[Formula 74]

[0134]

[Formula 75]

[0135]  
[Formula 76]

[0136]  
[Formula 77]

[0137]  
[Formula 78]

[0138]  
[Formula 79]

[0139]  
[Formula 80]

[0140]  
[Formula 81]

[0141]  
[Formula 82]

[0142]  
[Formula 83]

[0143]  
[Formula 84]

[0144]  
[Formula 85]

[0145]  
[Formula 86]

[0146]  
[Formula 87]

[0147]  
[Formula 88]

[0148]  
[Formula 89]

[0149]  
[Formula 90]

[0150]  
[Formula 91]

[0151]  
[Formula 92]

[0152]  
[Formula 93]

[0153]  
[Formula 94]

[0154]  
[Formula 95]



[0155]  
[Formula 96]

[0156]  
[Formula 97]

[0157]  
[Formula 98]

[0158]  
[Formula 99]

[0159]  
[Formula 100]

[0160]  
[Formula 101]

[0161]  
[Formula 102]

[0162]  
[Formula 103]

[0163]Organic coloring matter of this inventionF. M Harmer (F. M. Harmer)  
work "heterocyclic party \*\*\*\*\*- Cyanine Dyes and Related Compounds  
(Heterocyclic Compounds-Cyanine Dyes.) and Related Compounds"John Willie  
and Sons (John Wiley & Sons)-New YorkLondon1964 annual publicationsDay  
em Sturmer (D. M. Sturmer) work "heterocyclic Compounds-Special topics in  
heterocyclic chemistry (Heterocyclic Compounds-Special.) topics in  
heterocyclic chemistry"Chapter 18Section 14the 482nd to 515  
paragraphJohn Willie and Sons (John Wiley & Sons)-New YorkLondon1977  
annual publicationsROZZU chemistry OBU carbon party UNZU (Rodd's

Chemistry of Carbon Compounds) 2nd. Ed. vol. IV part B 1977 \*\*Chapter 15 the 369th to 422 paragraph ERUSEBIA science public company ink (Elsevier Science Publishing Company Inc.) company \*\*Based on a method of a statement it is compoundable to New York the British patent No. 1077611 etc.

[0164] A synthetic example is shown below.

[0165] Synthetic example 1. (composition of the compound I-1)

A compound (I-1) is compoundable according to the scheme 1 shown below.

[0166]

[Formula 104]

[0167] (A-1) Heat 10 g and 26.4 g of phenethyl PARATORU ene sulfonates at 160 \*\* for 5 hours. 25 ml of triethyl alt. propionate 25 ml of pyridine and 10 ml of acetic acid are added to the obtained quality of a brown candy-state object and it agitates at 150 \*\* for 1 hour. After radiational cooling ethyl acetate: If hexane = 1:3 solution is added and it agitates at a room temperature a \*\*\*\*\* oily matter will dissociate. The decantation washed 3 times by hexane except for the solvent. the obtained quality of a brown candy-state object -- methanol -- warming -- it dissolved and if the methanol solution of the sodium bromide 3.0 g is added and is settled overnight the crystal has deposited. a \*\* exception carries out a crystal by suction filtration -- methanol -- recrystallizing (I-1) -- 1.4 g was obtained.

( $\lambda_{\text{max}} = 507 \text{ nm}$  ( $\epsilon = 1.62 \times 10^5$ )) (inside of methanol)

[0168] Synthetic example 2. (composition of the compound I-17)

A compound (I-17) is compoundable according to the scheme 2 shown below.

[0169]

[Formula 105]

[0170] (A-2) Heat 10.8 g and 26.4 g of phenethyl PARATORU ene sulfonates at 160 \*\* for 5 hours. 40 ml of triethyl alt. propionate 50 ml of pyridine and 25 ml of acetic acid are added to the obtained quality of a brown candy-state object and it agitates at 135 \*\* for 0.5 hour. After radiational cooling ethyl acetate: If hexane = 1:4 solution is added and it agitates at a room temperature a \*\*\*\*\* oily matter will dissociate. The decantation washed 3 times by hexane except for the solvent. the obtained quality of a brown candy-state object -- methanol -- warming -- it dissolved and if the methanol solution of the sodium bromide 3.0 g is added and is settled overnight the crystal has deposited. a \*\* exception carries out a crystal by suction filtration -- methanol --

recrystallizing (I-17) -- 1.30g was obtained.

( $\lambda_{\text{max}} = 565 \text{ nm}$  ( $\epsilon = 1.26 \times 10^5$ )) (inside of methanol)

[0171] Synthetic example 3. (composition of compound II-1)

A compound (II-1) is compoundable according to the scheme 3 shown below.

[0172]

[Formula 106]

[0173] (A-1) Heat 10 g and 12-benzopropane Salton 12.2g at 160 \*\* for 5 hours. Ethyl acetate was added in the place cooled to 70 \*\* it agitated at the room temperature for 1 hour and the crystal was obtained. 20 ml of triethyl alt. propionate 20 ml of pyridine and 8 ml of acetic acid are added to this and it agitates at 150 \*\* for 1.5 hours. After radiational cooling if ethyl acetate is added and it agitates at a room temperature a \*\*\*\*\* oily matter will dissociate. the quality of a brown candy-state object obtained except for the solvent by the decantation -- methanol -- warming -- it dissolved and if triethylamine is added and it settles for 1 hour the crystal has deposited. a \*\* exception carries out a crystal by suction filtration -- methanol:chloroform = 1:1 solvent -- warming -- until it dissolves and solution volume becomes half -- ordinary pressure -- warming -- it condensed the crystal which deposited by settling overnight was taken out and (II-1) was obtained by drying. [ of 5.8g ] ( $\lambda_{\text{max}} = 504 \text{ nm}$  ( $\epsilon = 1.46 \times 10^5$ )) (inside of methanol)

[0174] Synthetic example 4. (composition of compound III-54)

A compound (III-54) is compoundable according to the schemes 4-6 shown below.

[0175]

[Formula 107]

[0176] Composition of a compound (A): Dissolve 20 g of 56-dichloro-2-methylbenzimidazole and 25.4 g of N-(2-bromoethyl) phthalimides in acetonitrile at a room temperature. It agitated at the room temperature for two days after dropping the solution of 4.4 g of sodium hydroxide at this. Dichloromethane extracted it dried and after carrying out decompression solvent distilling off a 44g crystal was obtained. 8 g of ethyl CHIRUPARA toluene sulfonates are added to the obtained crystal 10g and it agitates at 150 \*\* for 5 hours. After radiational cooling if acetone is added and it agitates at a room temperature a crystal deposits. The \*\* exception carried out the crystal by suction filtration and 13.0g (melting point of 289 \*\*) of compounds (1A) were obtained. 40 g of ethyl

CHIRUPARA toluene sulfonates were mixed with 30 g of 5-phenyl-2-methylbenzothiazole and it agitated at 150 °C for 5 hours. Crystallization was carried out with acetone after radiational cooling reduced pressure drying of the crystal was separated and carried out and 45g of white crystals were obtained. 3.8g picking and 4 g of NN'-diphenyl form amidines were added this was dissolved in ethanol and the heating rotary flow was carried out at 100 °C for 1 hour. When it cooled radiationally and reduced pressure drying of the precipitated crystal was separated and carried out 2.69g of compounds (2A) were obtained. 2.5 ml of acetic anhydrides and DMF 4ml were added to 1 g of compounds (2A) obtained as mentioned above and it agitated for 10 minutes at 100 °C. 1 g of compounds (1A) and 1.2 ml of triethylamine were added to this one by one and it agitated for 30 minutes at 100 °C. HARUTSU obtained by adding water after a reaction was taken out by the decantation it recrystallized with the methanol chloroform solvent and the compound (3A) was obtained. 230 ml of 31% of hydrobromic acid acetic acid solutions 100 ml of 49% of hydrobromic acid solution and 70 ml of trifluoroacetic acid were added to 7.0 g of obtained compounds (3A) and it returned for round three days at 130 °C. After carrying out vacuum concentration of the reaction mixture acetone was added and the crystal 4.9g ( $\lambda_{\text{max}} = 528 \text{ nm}$  ( $\epsilon = 5.68 \times 10^4$ )) of the compound (A) was obtained by separating a crystal and drying (inside of methanol).

[0177]

[Formula 108]

[0178] Composition of a compound (B): 11 g of 2-bromopropionamide was mixed with 20 g of 5-chloro-N-ethyl-2-methylbenzimidazole and it agitated at 160 °C for 6 hours. Crystallization was carried out with ethyl acetate the crystal was separated 100 ml of 49% of hydrobromic acid solution and 100 ml of water were added to this and the overheating rotary flow was carried out at 140 °C for 8 hours. After carrying out vacuum concentration of the reaction mixture acetone was added and the crystal 12g of the compound (1B) was obtained by separating a crystal and drying. 15 g of butane SARUTON was mixed with 20 g of 5-chloro-N-ethyl-2-methylbenzimidazole and it agitated at 160 °C for 6 hours. Crystallization was carried out with acetone the crystal was separated and it dried and the acetic anhydride was added in addition to this and the heating rotary flow of 20 g of the NN'-diphenyl form amidines was carried out at 150 °C for 6 hours. When it cooled radiationally and reduced pressure drying of the precipitated crystal was separated and

carried out 7.3 g of compounds (2B) were obtained. 2.2 g of compounds (1B) and compound (2B) 3g are melted at a room temperature in dimethyl sulfoxide and it is 1 and 8-diazabicyclo. 5[40] 3.1 ml of -7-undecene was added and it agitated at the room temperature for 1 hour. When the crystal deposited when ethyl acetate was added this was taken out and it recrystallized [ methanol ] 0.9 g ( $\lambda_{\text{max}} = 507 \text{ nm}$  ( $\epsilon = 6.97 \times 10^4$ )) of compounds (B) were obtained (inside of methanol).

[0179]

[Formula 109]

[0180] Composition of a compound (III-54): 100 mg of compounds (A) and 115 mg of compounds (B) were dissolved in 5 ml of dimethyl sulfoxide at the room temperature 30 mg of dimethylamino pyridine and 100 mg of 2-chloro-1-methylpyridinium iodide were added to this and it agitated for 20 minutes at the room temperature. 0.08 ml of triethylamine was added to this and it agitated at the room temperature further for 7 hours. Ethyl acetate was added the crystal was deposited silica gel column chromatography refined the obtained crystal and 20 mg ( $\lambda_{\text{max}} = 507.7 \text{ nm}$  ( $\epsilon = 1.39 \times 10^5$ )) of compounds (I-54) were obtained (inside of methanol).

[0181] Next the dye sensitizing optoelectric transducer adapting the poly methine coloring matter of this invention and a photogalvanic cell are explained in detail. In this invention a dye sensitizing optoelectric transducer is an electrode which consists of a layer (photosensitive layer) of the semiconductor particulate to which the poly methine coloring matter painted on a conductive substrate and a conductive substrate stuck. A photosensitive layer may be designed according to the purpose and monolayer composition or multilayered constitution may be sufficient as it. One kind or various mixing may be sufficient as the coloring matter in much more photosensitive layer. The light which entered into the photosensitive layer excites coloring matter. It has an energy-rich electron this electron is passed to the conducting zone of a semiconductor particulate from coloring matter and excitation coloring matter reaches a conductive substrate by diffusion further. Although the dye molecule serves as an oxidant at this time while the electron on an electrode works in an external circuit a photogalvanic cell returns to color-acid embodiment and a dye sensitizing optoelectric transducer works as a negative electrode of this cell.

[0182] A conductive substrate and a photosensitive layer are explained in detail below. A conductive substrate is a base material of glass or a

plastic which the base material itself will not have conductivity like metal or has a conducting agent layer on the surface. In the case of the latter as a desirable conducting agent metal carbon (for example platinum gold silver copper aluminum rhodium indium etc.) or conductive metallic oxides (what doped fluoride to an indium tin multiple oxide and tin oxide) are mentioned. A conductive substrate is so good that surface resistance is low. As a range of desirable surface resistance it is below 50 ohm/cm<sup>2</sup> and is below 10 ohm/cm<sup>2</sup> still more preferably. Substantially transparent thing of a conductive substrate is preferred. That it is transparent means substantially that transmissivity of light is not less than 10% it is preferred that it is not less than 50% and especially not less than 80% is preferred. What painted a conductive metallic oxide on glass or a plastic as a transparent conductive base material is preferred. As for light when using a transparent conductive base material it is preferred to make it enter from the base material side.

[0183] Semiconductor particulates are metal chalcogenides (for example lead oxide, lead sulfide, lead selenide etc.) or particles of perovskite. Preferably as metal being chalcogenide Titanium, tin, zinc, tungsten. An oxide of a zirconium, hafnium, strontium, indium, cerium, yttrium, lanthanum, vanadium, niobium or tantalum, cadmium sulfide, cadmium selenide etc. are mentioned. Strontium titanate, titanate, titanate, calcium etc. are mentioned preferably as perovskite. Titanium oxide, zinc oxide, tin oxide and especially tungsten oxide are [ among these ] preferred.

[0184] As a method of painting a semiconductor particulate on a conductive substrate, a method of applying dispersion liquid or a colloidal solution of a semiconductor particulate on a conductive substrate, a method of applying a precursor of a semiconductor particulate on a conductive substrate and moisture in the air hydrolyzing and obtaining a semiconductor corpuscle film etc. are mentioned. When compounding a method of distributing while grinding using a method and a mill which are mashed with a mortar as a method of creating dispersion liquid of a semiconductor particulate or a semiconductor, a method of depositing as particles and using it as it is in a solvent etc. are mentioned. As carrier fluid, water or various kinds of organic solvents (for example, methanol, ethanol, dichloromethane, acetone, acetonitrile, ethyl acetate etc.) are mentioned. In the case of distribution, polymer, a surface-active agent, acid or a chelating agent may be used as a distributed auxiliary agent if needed.

[0185] As for a semiconductor particulate, what has large surface area is preferred so that much coloring matter can be adsorbed. For example, it is preferred that the surface area is 10 or more times to a project area.

where a semiconductor particulate is painted on a base material and it is more preferred that they are 100 or more times. Since quantity of coloring matter which can be supported per unit area generally increases so that thickness of a layer of a semiconductor particulate is large, absorption-of-light efficiency becomes high but since the generated diffusion length of electron increases, a loss by electric charge recombination also becomes large. Although desirable thickness of a semiconductor particle layer changes with uses of an element, they are 0.1 micron thru/or 100 microns typically. When using as a photogalvanic cell, it is preferred that it is 1 thru/or 50 microns and it is more preferred that it is 3 thru/or 30 microns. A semiconductor particulate may be calcinated in order to stick particles after applying to a base material.

[0186] A method of immersing a semiconductor particulate often in a coloring matter solution dried to make coloring matter stick to a semiconductor particulate for a long time is common. A coloring matter solution may be heated at 50 °C thru/or 100 °C if needed. Adsorption of coloring matter may be performed before spreading of a semiconductor particulate or it may carry out after spreading. A semiconductor particulate and coloring matter may be applied simultaneously and may be made to adsorb. Washing removes unadsorbed coloring matter. When calcinating a coating film, it is preferred to perform adsorption of coloring matter after calcination. After calcination, before water sticks to the coating film surface, it is preferred especially to make coloring matter adsorb quickly. The number of coloring matter to which it sticks may be one and several sorts may be mixed and it may be used. When mixing, may mix the poly methine coloring matter of this invention and A U.S. Pat. No. 4927721 item A complex pigment of a statement and coloring matter of this invention may be mixed on No. 4684537, No. 5084365, No. 5350644, No. 5463057, No. 5525440 and JP7-249790A specifications. When a use is a photogalvanic cell, coloring matter mixed so that a wavelength band of photoelectric conversion may be made large as much as possible is chosen. Co-adsorption of the colorless compound may be carried out for the purpose of reducing an interaction of coloring matters such as a meeting. A steroid compound (for example, cholic acid) etc. which have a carboxyl group as a hydrophobic compound which carries out co-adsorption are mentioned.

[0187] as for the coloring matter amount of adsorption to a semiconductor particle layer in this invention, it is preferred that they are the \*\*\*\* hit 0.01 of a coating film - 100 mmol as a total amount of coloring matter -- more -- desirable -- a \*\*\*\* hit -- they are the \*\*\*\* hit 0.5 -

20mmol still more preferably 0.1 to 50 mmol.

[0188]After adsorbing coloring matter amines may be used and the surface of a semiconductor particulate may be processed. As desirable amines pyridine 4-tert-butylpyridine polyvinyl pyridine etc. are mentioned. In the case of a fluid it may use as it is and these may dissolve and use it for an organic solvent.

[0189]Thus a created dye sensitizing optoelectric transducer is applicable to various kinds of sensors and photogalvanic cells. When applying to a photogalvanic cell a charge transfer layer and a counterelectrode are required. Hereafter a charge transfer layer and a counterelectrode are explained in detail. A charge transfer layer is a layer which has the function to supplement an oxidant of coloring matter with an electron. What is called a gel electrolyte with which a polymer matrix was impregnated in a fluid which dissolved a redox couple in an organic solvent as a typical example and a fluid which dissolved a redox couple in an organic solvent fused salt containing a redox couple etc. are mentioned. as a redox couple -- for example iodine and an iodide (for example a lithium iodide and iodination tetrabutylammonium.)

Combinations such as iodination tetrapropylammonium alkyl viologen (for example methyl viologen chloride hexyl viologen bromide benzyl viologen tetrafluoroborate) and its reduced form should put together. Polyhydroxy benzenes (for example hydroquinone naphthohydroquinone etc.) and an oxidant of those should put together. Combination of a divalent and trivalent iron complex (for example red prussiate of potash and yellow prussiate of potash) etc. are mentioned. Combination of iodine and an iodide is [ among these ] preferred. As an organic solvent which melts these aprotic polar solvents (for example acetonitrile propylene carbonate ethylene carbonate dimethylformamide dimethyl sulfoxide sulfolane 1,3-dimethyl imidazolinone 3-methyl oxazolidinone etc.) are preferred. Polyacrylonitrile a polyvinylidene fluoride etc. are mentioned as polymer used for a matrix of a gel electrolyte. By mixing polyethylene oxide with a lithium iodide as fused salt to at least one kind of other lithium salt (for example lithium acetate lithium perchlorate etc.) what gave mobility in a room temperature is mentioned. Concentration of a grade which becomes an electronic carrier is required for a redox couple. As desirable concentration in total it is 0.01 mol/l. or more is 0.1 mol/l. more preferably and is 0.3 mol/l. or more especially preferably.

[0190]A counterelectrode works as an anode of a photogalvanic cell. Although a counterelectrode is usually synonymous with the above-mentioned conductive substrate with composition that intensity is fully



maintained a base material is not necessarily required. However it is more advantageous to have a base material in respect of sealing nature. In order for light to reach a photosensitive layer at least the above-mentioned conductive substrate and one side of a counterelectrode must be substantially transparent. In a photogalvanic cell of this invention a conductive substrate is transparent and it is preferred to enter sunlight from the base material side. In this case as for a counterelectrode it is still more preferred to have the character to reflect light. Glass which vapor-deposited metal or a conductive oxide as a counterelectrode of a photogalvanic cell or a plastic is preferred and especially glass that vapor-deposited platinum is preferred. [0191] In order to prevent evapotranspiration of a structure in a photogalvanic cell it is preferred to seal the side of a cell with polymer adhesives etc.

[0192]

[Example] Although an example explains concretely the dye sensitizing optoelectric transducer of this invention and the preparation method of a photogalvanic cell below this invention is not limited to these.

[0193] The preparation inside of example 1 titanium-dioxide dispersion liquid to the vessel made from stainless steel with a content volume of 200 ml which carried out Teflon coating 15 g of titanium dioxides (Japanese Aerosil Degussa P-25) The water 45 g 1 g of dispersing agents (the Aldrich make Triton X-100) and 30 g of zirconia beads (made by Nikkato Corp.) 0.5 mm in diameter were put in and it distributed at 1500 rpm for 2 hours using the Sand grinder mill (made by eye MEKKUSU). Zirconia beads were filtered and removed from the dispersed matter.

[0194] The glass rod was used and the above-mentioned dispersion liquid were applied to the electric conduction side side of the electrically conductive glass (what carried out cut processing of the Asahi Glass TCO glass to the size of 20 mm x 20 mm) which coated the tin oxide which doped the creation fluoride of the optoelectric transducer. Under the present circumstances adhesive tape was stretched to the part (from an end to 3 mm) by the side of an electric conduction side and it was considered as the spacer and glass was put in order and it applied eight sheets at a time at once so that adhesive tape might come to both ends. Air-drying and adhesive tape were removed for one day at the room temperature after spreading. (The portion with adhesive tape being used in the case of photoelectric conversion measurement in order to take a measuring instrument and electric contact) next this glass were put into the electric furnace (Yamato Scientific muffle furnace FP-32 type) and it calcinated for 30 minutes at 450 \*\*. The ethanol solution  $\{6 \times 10^{-4} \text{ mol /}$

liter of the coloring matter of this invention shown in Table 1 after taking out glass and cooling [Each  $3 \times 10^{-4}$  mol/liter coloring matter expressed with general formula (I) and general formula (II)] It was immersed in} for 3 hours. After the glass which coloring matter dyed was immersed in the 10% ethanol solution of 4-tert-butylpyridine for 30 minutes natural seasoning was washed and carried out by ethanol.

[0195] The optoelectric transducer of the creation above of the photogalvanic cell was piled up with the platinum vacuum evaporation glass of the same size as this (it has shifted so that the non-application portion of an optoelectric transducer may not be contacted on platinum vacuum evaporation glass). Next the electrolysis solution (0.05 mol/l. of iodine the solution of 0.5 mol/l. of lithium iodides which used the mixture of the volume ratio 90 to 10 of acetonitrile and N-methyl-2-oxazolidinone as the solvent) was infiltrated into the crevice between both glass using capillarity.

[0196] The imitation sunlight which does not include ultraviolet rays was generated by letting AM1.5G filter (made by Oriel) and a sharp cut filter (Kenko L-42) pass for the light of the xenon lamp (made by USHIO) of the measurement 500W of photoelectric conversion efficiency. This luminous intensity was 50 mW/cm<sup>2</sup>. The optoelectric transducer of this invention was irradiated with this light and the generated electrical and electric equipment was measured with the current potential measuring device (case rhe 238 type). The open circuit voltage of the photogalvanic cell called for by this a short-circuit current a form factor and conversion efficiency were summarized in Table 1.

[0197]

[Table 1]

[0198] The optoelectric transducer produced by the way having used the ethanol solution { $3 \times 10^{-4}$  mol/liter} of the coloring matter of this invention shown in the following table 2 instead of the coloring matter of Table 1 in the example 2 above-mentioned example 1 at the time of creation of an optoelectric transducer only differ. And the open circuit voltage the short-circuit current the form factor and conversion efficiency which measured the photogalvanic cell like Example 1 were summarized in Table 2.

[0199]

[Table 2]

[0200]The photoelectric transfer characteristic in which any coloring matter of this invention is more expensive than conventional coloring matter is accepted as shown in Example 1 and Example 2.

[0201]

[Effect of the Invention]It became clear that the dye sensitizing optoelectric transducer using the organic coloring matter which has a high photoelectric transfer characteristic by this invention is provided.

(19) 日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11) 特許出願公開番号

特開平11-167937

(43) 公開日 平成11年(1999) 6 月22日

(51) Int.Cl.<sup>6</sup>  
H 0 1 M 14/00  
H 0 1 L 31/04

識別記号

F I  
H 0 1 M 14/00 P  
H 0 1 L 31/04 Z

審査請求 未請求 請求項の数6 O L (全114頁)

(21) 出願番号 特願平10-241839

(22) 出願日 平成10年(1998) 8 月27日

(31) 優先権主張番号 特願平9-267455

(32) 優先日 平 9 (1997) 9 月30日

(33) 優先権主張国 日本 (J P)

(31) 優先権主張番号 特願平9-281187

(32) 優先日 平 9 (1997) 9 月30日

(33) 優先権主張国 日本 (J P)

(71) 出願人 000005201

富士写真フイルム株式会社

神奈川県南足柄市中沼210番地

(72) 発明者 小林 克

神奈川県南足柄市中沼210番地 富士写真  
フイルム株式会社内

(72) 発明者 日置 孝徳

神奈川県南足柄市中沼210番地 富士写真  
フイルム株式会社内

(72) 発明者 山下 克宏

神奈川県南足柄市中沼210番地 富士写真  
フイルム株式会社内

(74) 代理人 弁理士 萩野 平 (外4名)

最終頁に続く

(54) 【発明の名称】 光電変換素子

(57) 【要約】

【課題】 高い光電変換特性を有する有機色素を用いた色素増感光電変換素子を提供する。

【解決手段】 有機色素によって増感された半導体微粒子を用いる光電変換素子であって、半導体微粒子表面に対し垂直方向に色素発色団が複数個存在するように有機色素が吸着していることを特徴とする光電変換素子。ただし、金属多核錯体部分は一つの発色団とする。